JOURNAL OF MATERIALS SCIENCE **38** (2003) 4319– 4323

CO gas sensors operating at room temperature

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Carbon monoxide (CO) gas sensors operating at room temperature were fabricated using rutile tin oxide and hexachloro-platinic acid to get a high dispersion rate of platinum in the tin oxide. The sensor material was analyzed by EDS, TG/DTA, SEM and FTIR. The number of chemisorbed atom per unit area and sensor sensitivity were related by space charge model. Gas sensing characteristics were investigated as a function of Pt content, heat-treatment temperature and operating temperature. The humidity dependence of the fabricated sensors is also discussed. © *2003 Kluwer Academic Publishers*

1. Introduction

Detection of toxic and flammable gases is a subject of growing importance in both domestic and industrial environments. The atmospheric pollution has lead to the research and development of a variety of sensors using different materials and technologies particularly for low cost and a lower operating temperatures [1, 2].

Semiconductor sensors are used as sensors of reduced gases like H_2, CO, hydrocarbon and other organic gases and vapors. The *n*-type semiconductor sensors normally operate by adsorption of oxygen that leads to a high resistance, and the resistance is lowered when a reducing gas reacts with the adsorbed oxygen. Depending on the temperature, the reducing agent may react with either adsorbed or lattice oxygen. This reaction may proceed via the catalyst supported on the semiconductor sensor rather than directly on the semiconductor surface. The choice of a given *n*-type semiconductor oxide depends on its properties. Tin oxide is currently the prime choice because it is chemically stable, its electron mobility is relatively high, and the donor density varies many orders of magnitude, depending on its source and thermal history [2–6]. Tin oxide assumes a bulk oxygen deficiency upon high temperature calcination that results in a reasonably low resistance in the flat band condition.

The operating temperature used is determined by many considerations, such as the power dissipation, the type of catalyst used and the selectivity [7]. For a practical device one wishes to minimize the power needed to operate, so the lowest practical temperature is desired. In an atmosphere containing flammable gases, a low temperature is favored also for safety. The sensor, however, must be heated enough so that catalytic oxidation of the gas of interest is possible. Thus, sensors often operate between 250 and 350°C, a temperature range determined based on a compromise between the above limitations. Another consideration is humidity; the lower the humidity, in general, the greater the dependency to relative humidity [1]. Therefore, there is a need to develop CO sensors that have a relatively high sensitivity at the low temperatures and do not depend on the relative humidity. In this paper, the sensing characteristics of a SnO_2-based CO gas sensor operating at room temperature is reported.

2. Experimental

Gas sensors were fabricated through the conventional ceramic process. We used tin oxide rutile as the sensor material and hexachloro-platinic acid($H_2PtCl_6{\cdot}6H_2O$) as additive. Hexachloro-platinic acid was used to add Pt of various mass ratio (0, 0.5, 1, 2 wt%) and to get a high dispersion rate. Because hexachloro-platinic acid is easily soluble in water, it mixes well with SnO_2 better than Pt powder or platinum oxide. SnO_2 powder with added $H_2PtCl_6{\cdot}6H_2O$ was mixed with D.I water and ground in attrition mill for 1 h to get the fine particles. The slurry was sieved and treated at 120°C for 6 h in drying oven and it was ground in an agate mortar with polyvinyl alcohol. Prepared mass was sieved using 100 μm sieve and molded at 3000 psi pressure. The samples were sintered at 600, 700 and 800°C, respectively, in air for 1 h. To measure the electrical characteristics, the electrodes were formed using Ag/Pd paste by the screen printing method and electrical lead wires were attached on the opposite sides of the rectangular type device.

Fig. 1 shows the measurement setup of gas sensing characteristics. The chamber is located inside a high-speed drying oven that helps set up the operating temperature. MFCs control the input gas concentrations and humidity through dry air, vapor saturator and CO gas columns.

3. Results and discussions

When the CO gas is adsorbed on the surface of an oxide semiconductor, the gas-solid system can be postulated similar to a metal-semiconductor contact. At equilibrium, we can assume: (i) every adsorbed atom captures one electron, (ii) concentration of singly ionized defects is the same in the interior and in the boundary layer, and (iii) the free carrier concentration is assumed

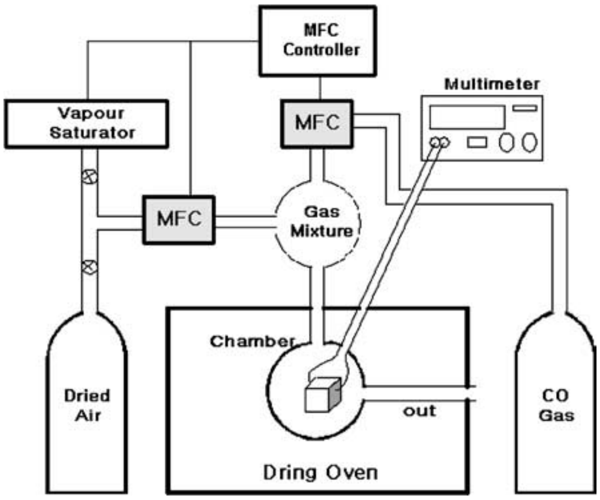

Figure 1 Apparatus for measurement.

to fall abruptly from the bulk to the space charge region. The number of chemisorbed atom per unit area is

$$N_g = Wn_e(w) \tag{1}$$

where W is the depth of the space charge region and n_e is the number of electron per unit volume. From Poisson equation, the potential distribution of semiconductor surface and the space charge region width can be obtained as

$$\phi(x) = -\frac{qn_e(w)}{2\varepsilon_s}w^2\left(1 - \frac{x}{w}\right)^2 \tag{2}$$

$$W = \left(\frac{2\varepsilon_s}{qn_e(w)}\phi_0\right)^{\frac{1}{2}} \tag{3}$$

where q is an electron charge, ε_s is the dielectric constant and ϕ_0 is the potential at the surface ($x = 0$). Therefore, Equation 1 becomes

$$N_g = \left(\frac{2\varepsilon_s n_e(w)\phi_0}{q}\right)^{\frac{1}{2}} \tag{4}$$

If every donor defect level in the n-type semiconductor injects its electron to the conduction band, $n_e(w)$ becomes donor concentration N_d. For SnO_2, N_g is about $1.42 \times 10^{12}/\text{cm}^2$. The number of atoms in the surface of metal oxide is about 10^{15}, so that the coverage for depletive adsorption is less than 1%.

The sensitivity to a reduced gas, defined as the ratio of resistance difference in the presence and in the absence of the traget gas, is expected to depend on the increase of the number of carriers in the presence of the gas [7]. From Morrison's report [8], the number of chemisorbed atom per unit area is proportional to square root of the partial pressure of the reduced gas. The sensor sensitivity can be expressed as

$$\frac{\Delta R}{R_0} = \gamma P_g^{1/2} - 1 \tag{5}$$

where $\Delta R/R_0$ is the ratio of resistance difference in the presence and in the absence of reduced gas, P_g is the partial pressure of the reduced gases and γ is a constant.

Quantitative analysis of the SnO_2/Pt sample was characterized using energy dispersive X-ray spectroscopy (Kevex sigma MS2). Fig. 2 shows the spectrum of 1 wt% Pt doped-SnO_2 sample. Sn peak and Pt peak were dispersed uniformly on the surface, and at.% of Pt was determined to be 1.13 (Table I). This occurs because the mixed Pt was partially oxidized and/or oxygen ions in the air were adsorbed on the adsorption site of Pt. This also suggests that the spillover of oxygen ions from Pt to SnO_2 occurs that is needed for sensing.

The weight loss and phase transformation of SnO_2/Pt compound was investigated by TG/DTA. Fig. 3 shows the TG/DTA curves of starting material, SnO_2 added with $H_2PtCl_6{\cdot}6H_2O$. The sample was measured in an alumina cup to minimize the change of baseline. The heating rate was 10°C/min and the flow rate of air was 1 l/min, respectively. Endothermic reaction was

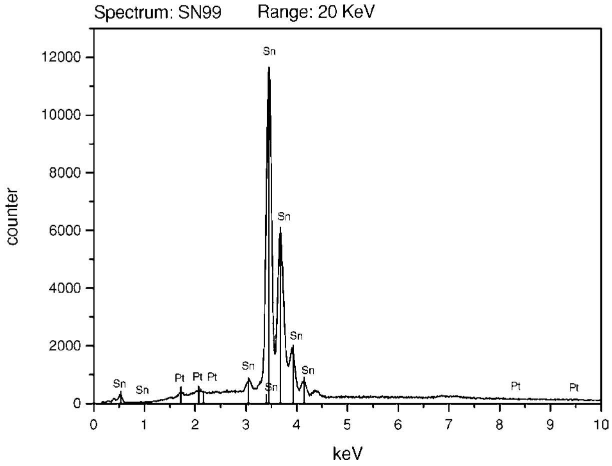

Figure 2 EDS spectrum of 1 wt% Pt doped-SnO_2 sample.

TABLE I EDS analysis data

Element	Line	Weight%	K-Ratio	Cnts/s	Atomic%
Sn	La	98.15	0.9700	1339.22	98.87
Pt	La	1.85	0.0163	2.90	1.13

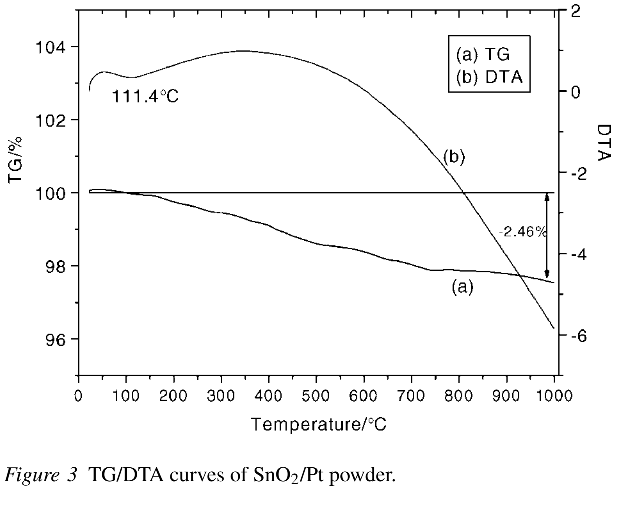

Figure 3 TG/DTA curves of SnO_2/Pt powder.

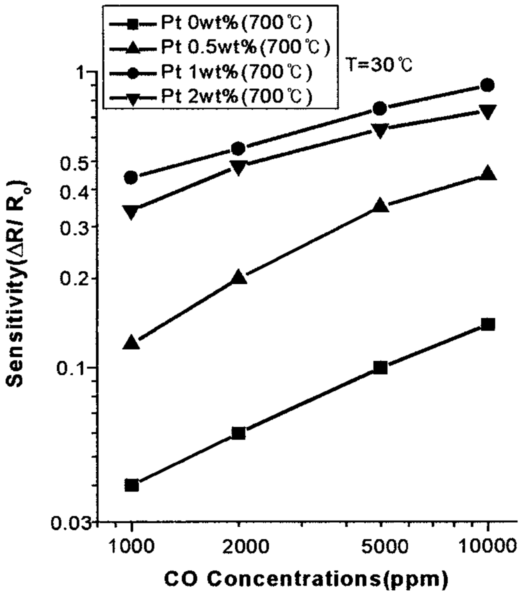

Figure 4 CO sensitivity as a function of Pt content.

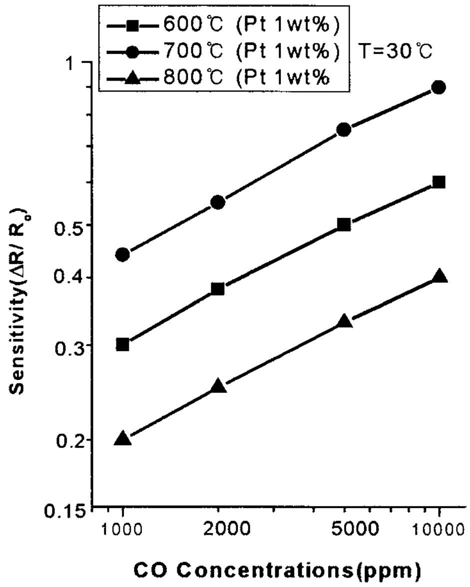

Figure 5 CO sensitivity as a function of heat-treatment temperatures.

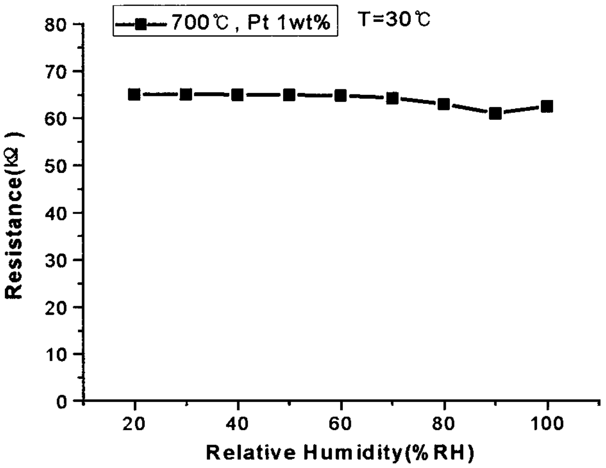

Figure 7 Humidity dependence of the device.

observed at 111.4°C based on the DTA curve. This reaction is caused by the vaporization of water molecules and organic materials such as poly vinyl alcohol. The decomposition temperature of the hexachloro-platinic acid is around this temperature. TG curve shows weight loss starting at 100°C to 700°C. Weight loss is about 2.46% at 1,000°C. No phase transformation of SnO_2/Pt could be found up to 1000°C. Thus, the prepared powder should be stable around 700°C.

Catalysis is a key factor in semiconductor sensors. Catalysts are added to the host material to speed up the reaction, to impart selectivity to the sensor, and to lower the operating temperature [1]. The metal dispersion can be characterized in terms of metal surface area and average metal particle size. H. Gruber [9] studied gas adsorption on unsupported and supported platinum using the BET method. He reported that the dispersion of chloroplatinic acid impregnation (surface area: 229 m^2/g, particle size: <10 Å) is much higher than that of Pt black (surface area: 2.4 m^2/g, particle size: 800 Å) in Pt/η-Al_2O_3 system. Fig. 4 represents the CO sensitivity ($= \Delta R/R_0$, where ΔR is the resistance difference between in air and in the test gas, and R_0 is the resistance in air) characteristics as a function of wt% Pt which was obtained by varying the concentration of hexachloro-platinic acid. The measuring temperature inside the test chamber was 30°C. SnO_2 sensor without Pt showed very low sensitivity, however, 1 wt% Pt-doped SnO_2 sensor exhibited the highest sensitivity to CO gas. The sensor sensitivity was proportional to square root of CO gas concentration according to Equation 5.

Fig. 5 shows CO sensitivity variation of the sensors as a function of heat-treatment temperature for devices held at constant 30°C operating temperature. The highest response is obtained for 700°C heat-treated sample. Fig. 6 shows SEM (Hitachi S-4200) micrographs of samples heat-treated at 600°C (a), 700°C (b) and 800°C (c). No remarkable change of surface morphology was

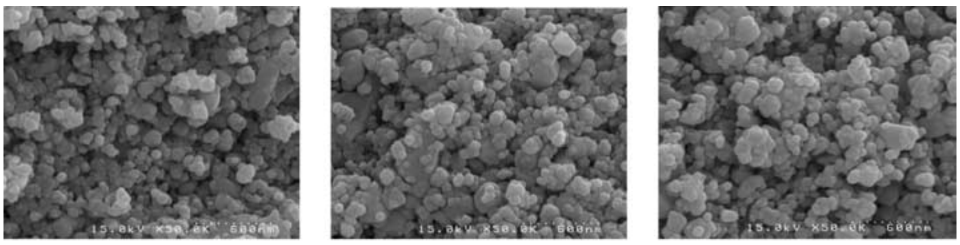
(a) (b) (c)

Figure 6 SEM micrographs of SnO_2/Pt ceramics annealed at (a) 600°C, (b) 700°C and (c) 800°C in air for 1 h.

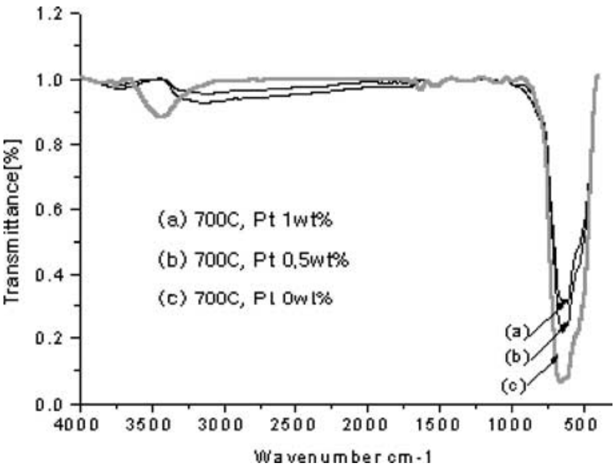

Figure 8 IR absorbance spectrum of the samples: (a) 1 wt% Pt doped SnO_2, (b) 0.5 wt% Pt doped SnO_2 and (c) undoped SnO_2.

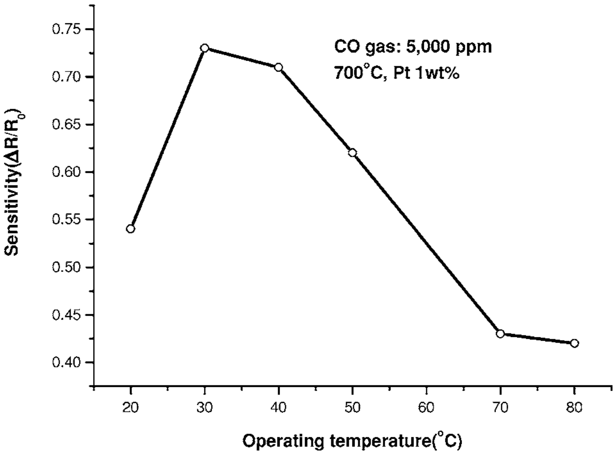

Figure 9 Influence of the operating temperature of SnO_2/Pt sensor on the sensitivity.

observed between Fig. 6a and b. However, some grain growth of SnO_2 particles was found to occur during heat-treating at 800°C, as shown in Fig. 6c. This grain growth leading to the reduction of the surface area is responsible for low sensitivity. The sample annealed at 700°C is preferred for CO gas sensor applications.

Yannopoulos [10] suggests that the sensitivity change with humidity, when the sample is used as a CO sensor, is due to the water/gas reaction, leading to a CO/H_2 ratio in the gas that depends on the water vapor pressure. Both oxygen ion and hydroxyl group attached to unsaturated tin sites donate electron to SnO_2 by reaction with a reducing gas. However, hydroxyl groups are blocked by water molecules at low temperature and high humidity because of water condensation on the sensor surface [11]. Fig. 7 shows the humidity dependence of fabricated ceramic CO sensor. We can see that this device is relatively insensitive to humidity in the humidity range from 20% RH to 100% RH, although sensor resistance decreases above 70% RH because of instability from water condensation.

IR absorbance intensity at 3200–3700 cm^{-1} vibration band (O—H) region becomes lower in the sample containing more platinum as additive as shown in Fig. 8. McAleer *et al.* [12] showed by a simple resistance measurement how much more effectively oxygen increases the resistance of a pressed SnO_2 pellet in moist air when a catalyst (Pd or Pt) is present or not. They concluded that the resistance is orders of magnitude higher with the catalyst, presumably providing oxygen by spillover effect. However, without the catalyst, water molecules dominate, injecting electrons by forcing oxygen desorption. It is seen that Pt incorporation helps the oxygen ion to occupy the unsaturated tin sites and the oxidation of the adsorped CO can be accelerated on the tin oxide by dispersed metallic platinum. It is possibility that hydroxylated surface reduces as Pt content increases [13]. The strong absorbance intensity of Sn—O band is also observed at 450–800 cm^{-1} range.

Fig. 9 shows the dependence of CO gas sensitivity of SnO_2/Pt sensor on the operating temperature in the range of 20°C to 80°C. The operating temperature range that has the highest sensitivity was found to be 30–40°C. Korotchenkov *et al.* [2] suggested that sensors need the combination of bulk and surface doping and better catalytic ability to reduce the operating temperature. We can see that SnO_2 sensor doped hexachloro-platinic acid has the highest efficiency of CO oxidation and less activation energy of CO and oxygen adsorption.

Fig. 10 shows the response of Pt/SnO_2 system to CO gas at two different temperatures. The data

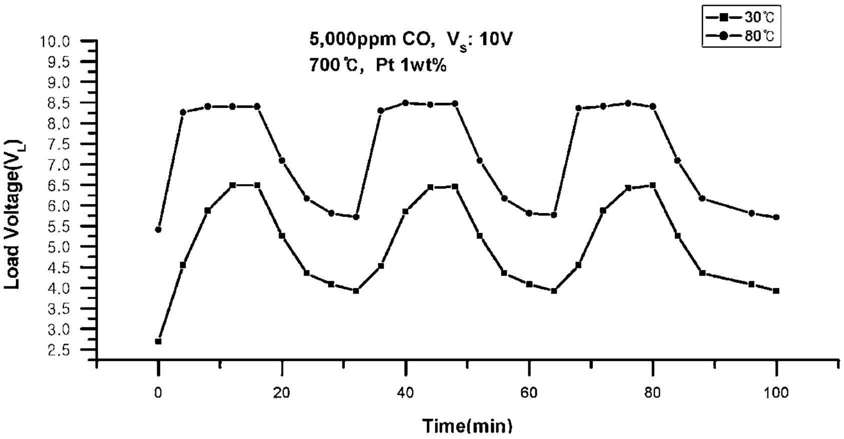

Figure 10 Sensor response to CO gas at 30°C and 80°C.

demonstrates that the sensor can operate at these low temperatures in a reasonably recoverable manner. The response time is understandably long (∼12 min at 30°C) because of the low temperature. However, for applications where gas composition doesn't change within such time interval, this sensor is expected to perform satisfactorily. The role of SnO_2 defects in the sensor response is believed to be suppressed at these relatively low temperatures, but defects are probably important as they act as local adsorption or reaction sites, for determining the absolute conductance level and for understanding the drift problems that occur during high temperature operations [14].

4. Conclusions

CO gas sensors operating at room temperature were fabricated using tin oxide rutile as the host material and hexachloro-platinic acid as a catalyst additive. The sample exhibited the highest sensitivity to CO gas at Pt content of 1 wt% and at 700°C annealing condition. The sensor sensitivity was proportional to square root of CO gas concentration consistent with the proposed model. This device is relatively insensitive to humidity in the humidity range from 20% RH to 100% RH. It is observed that IR absorbance intensity at 3200–3700 cm^{-1} vibration band (O—H) region becomes lower in the sample containing more platinum as additive.

Acknowledgment

The authors wish to acknowledge the financial support of Kyungnam University made in the program year of 2003.

References

1. M. J. MADAOU and S. R. MORRISON (Academic Press, New York, 1989) p. 493.
2. G. S. KOROTCHENKOV, S. V. DMITRIEV and V. I. BRYNZARI, *Sens. Actuators* B **54** (1999) 202.
3. K. D. SCHIERBAUM, U. WEIMAR and W. GOPEL, *ibid.* **7** (1992) 709.
4. N. YAMAZOE, Y. KUROKAWA and T. SEIYAMA, *ibid.* **4** (1983) 283.
5. K. ZAKRZEWESKA, *Thin Solid Films* **391** (2001) 229.
6. G. ZHANG and M. LIU, *Sens. Actuators* B **69** (2000) 144.
7. R. K. SRIVASTAVA, P. LAL, R. DWIVEDI and S. K. SRIVASTAVA, *ibid.* **21** (1994) 213.
8. S. R. MORRISON, *ibid.* **12** (1987) 425.
9. H. L. GRUBER, *J. Phys. Chem.* **66** (1962) 48.
10. L. N. YANNOPOULOS, *Sens. Actuators* **12** (1987) 77.
11. N. D. PARKYNS, *J. Chem. Soc.* A (1969) 410.
12. J. F. McALEER, P. T. MOSELEY, J. O. W. NORRIS, D. E. WILLIAMS and B. C. TOFIELD, in Proceedings of 2nd IMCS, Bordeaux, France (1986) p. 264.
13. H. DU, X. YAO and L. ZHANG, *Ceramic Int.* **28** (2002) 231.
14. S. SEMANCIK and T. B. FRYBERGER, *Sens. Actuators* B **1** (1990) 97.

Received 24 March
and accepted 24 July 2003